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(57) Abstract

Articles are shaped or formed, typically by thermoforming a sheet material, from a thermoplastic composition comprising (i) at least one polyester containing diol residues comprising ethylene glycol residues and diacid residues comprising terephthalic acid residues, 2,6-naphthalene-dicarboxylic acid resides or a mixture thereof; and (ii) certain epoxy-containing impact modifiers. Food trays which exhibit improved impact strength, particularly at low temperatures, represent a preferred embodiment of the articles.

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POLYESTER ARTICLES HAVING IMPROVED IMPACT STRENGTH

Field of the Invention

This invention pertains to articles shaped or formed from sheet extruded from certain polyester compositions that exhibit improved impact strength, particularly at low temperatures. More specifically, this invention pertains to novel articles fabricated, typically by thermoforming a sheet material, from a thermoplastic composition comprising (i) at least one polyester containing diol residues comprising ethylene glycol residues and diacid residues comprising terephthalic acid residues, 2,6-naphthalenedicarboxylic acid resides or a mixture thereof; and (ii) certain epoxy-containing impact modifiers. Food trays (containers) which may be subjected to low temperatures (refrigeration) are a preferred embodiment of the present invention.

Background of the Invention

Polyethylene terephthalate (PET) is a material commonly extruded into sheet (including film) of between 100 and 1000 microns thick. Such sheet material may be used as-fabricated or shaped, e.g., by thermoforming, into articles such as displays, signs, credit or debit cards, or packaging articles. For example, extruded PET sheet material can be used to make trays, packages or containers in which frozen foods can be both stored and heated and/or cooked in an oven. As used herein, the terms tray or trays are intended to include packages and containers in which food, especially frozen food, is packaged and sold for subsequent heating and/or cooking while still in the tray, package or container. Food trays fabricated from crystallized PET retain good dimensional stability over the range of temperatures commonly encountered during both microwave and convection oven cooking. Polyester food trays are conveniently manufactured by first extruding a sheet of polyester, then thermoforming

the tray in a heated die. This thermoforming process both forms the tray and crystallizes the polyester resin. The sheet material may be prepared in a process separate from the thermoforming process (sometimes referred to as the glass to mold process) or the sheet material may be prepared in-line with the thermoforming process (sometimes referred to as the melt to mold process). Processes for extruding polyester sheeting and thermoforming the sheet material to produce crystalline PET (also commonly known as CPET) food trays are well known in the art.

One problem encountered with PET food trays is that they occasionally break when trays containing frozen food are dropped. One way to improve the low temperature toughness of the trays is to use high molecular weight PET in the fabrication of the tray. Therefore, PET used in food trays often is specially manufactured to produce intrinsic viscosities (IV's) of 0.90 to 1.05 dL/g. Another approach is to add an impact modifier to the PET during the sheet extrusion process. In general. the trays are toughest when both approaches are utilized.

U.S. Patent 3,960,807 discloses the use of a "crack stopping agent" to improve the toughness of CPET trays. This crack stopping agent may be a polyolefin or other thermoplastic material present in concentrations of 2-16 weight percent. The tray compositions of U.S. 3,960,807 also contain 0.01–20 weight percent of an inorganic nucleating agent. U.S. Patents 4,463,121 and 4,572,852 disclose that the inorganic nucleating agent employed in the compositions of the '807 patent are unnecessary and that the polyolefin also can serve as a nucleating agent. These patents disclose that various crystallization aids often are added to the PET during the extrusion of the sheet material In order to control the crystallization rate of the PET. These crystallization aids may be organic compounds, such as polyolefins according to the disclosure of U.S. 4,463,121, or inorganic compounds. such as talc according to the disclosure of U.S. 3,960,807.

U.S. Patent 4,713,268 discloses that the toughness of food trays when impacted at −18°C (0°F) is greatly improved by the addition of a core-shell impact modifier. These impact modifiers consist of a core of either butadiene methacrylate-butadiene-styrene (MBS) or butyl acrylate (acrylic) and a methyl methacrylate shell. The system described in the '268 patent also includes 1-5 weight percent aromatic polyester crystallization rate enhancer and 0-14.5 weight percent aromatic polycarbonate. U.S. Patent 5,322,663 discloses that ethylene/methyl acrylate, ethylene/ethyl acrylate and ethylene/vinyl acetate copolymers may be used instead of linear low density polyethylene (LLDPE) as a nucleating agent in order to overcome plate-out problems associated with the use of LLDPE. This patent does not provide any evidence, however, that these copolymers are effective nucleating agents. The '663 patent also teaches that the copolymers are effective impact modifiers at ambient (room) temperature but are not effective as impact modifiers at low temperatures. The patent suggests, therefore, that the impact modifiers described in the '268 patent should be used in addition to the copolymers described in the '663 patent.

Published PCT Patent Application WO 93/15146) discloses the use of various non-functionalized poly(alkyl acrylates) to toughen CPET food trays. These poly(alkyl acrylate) materials may be used alone or in combination with an acrylic core-shell impact modifier. U.S. Patent 5,382.628) discloses the use of polymers or copolymers made from 1.4-cyclohexanedimethanol to toughen CPET food trays.

The following patents disclose the use of core/shell impact modifiers as toughening agents for polyesters. U.S. Patents 4,180,494 and US 4,264,487 describe the compositions of matter used in U.S. Patent 4,713,268 for food trays. U.S. Patent describes compositions comprising butadiene core/methyl methacrylate (MMA) or styrene shell impact modifiers and polyesters. U.S. Patent 4,034,013 describes compositions

comprising butyl acrylate core/epoxide-containing MMA shell impact modifiers and polyesters.

U.S. Patent 4,096,202 describes compositions comprising butyl acrylate core/non-functionalized MMA shell impact modifiers and polyesters. U.S. Patent 4,180,494 describes compositions comprising a butadiene core/MMA shell (acrylic) impact modifier, 1-8% polycarbonate compatibilizing agent, and a polyester. U.S. Patent 4,264,487 describe compositions comprising a butyl acrylate core/MMA-sytrene shell (MBS) impact modifier, 1-8% polycarbonate compatibilizing agent, and a polyester. U.S. Patent 5,652,306 and European Patent Publication EP 737,715 A2 discloses compositions comprising either a MBS- or acrylic- type core/shell impact modifier and small amounts of ethylene/alkyl acrylate/GMA terpolymers.

The following patents describe the general use of alkyl acrylates, epoxide-containing alkyl acrylates, and epoxide-containing polyolefins as toughening agents for polyesters. U.S. Patents 3,562,200 and 3,578,729 describe polyesters containing non-functional poly(alkyl acrylates). U.S. Patent 3,591,659 describes polyesters which contain esters of acrylic acid, methacrylic acid or ethacrylic acid as toughening agents. U.S. Patent 4,172,859 lists a variety of functional groups that can be grafted or copolymerized onto ethylene-based elastomers for use with polyesters and nylons.

U.S. Patent 4,284,540 describes the use of ethylene/glycidyl methacrylate (GMA) copolymers as a toughening agent for polyesters when combined with 0.1 to 5 weight percent of a barium catalyst. This patent also notes that ethylene/GMA copolymers increases the crystallization rate of PET and that PET containing antimony catalyst residues produces the best reaction with epoxy containing materials.

U.S. Patent 4,753.980 discloses that polyester compositions containing 3-40 weight percent of either ethylene/ethyl acrylate/GMA

terpolymer or ethylene/butyl acrylate/GMA terpolymer possess superior low temperature toughness when compared to analogous polyester compositions which contain an ethylene/methyl acrylate/GMA terpolymer. U.S. Patent 4,912,167 discloses polyester compositions containing a combination of an ethylene/butyl acrylate/GMA terpolymer and a zinc salt catalyst which exhibit improved blow molding properties. European Patent Publication EP 481,471 B1 and Penco et al., *Journal of Applied Polymer Science,* 57, 329 (1995) describes the use of a combination of linear low density polyethylene, an ethylene/ethyl acrylate/GMA terpolymer and 0.5% to 1% of an amine for the opening of an epoxy ring. U.S. Patents 5,098,953, 5,086,119, 5,086,118, 5,086,116, and 5,068,283 disclose that the toughness of polyester compositions containing ethylene/GMA copolymers or ethylene/alkyl acrylate/GMA terpolymers can be improved by the inclusion of a functional crosslinking agent in the compositions. The functional crosslinking agent contains, in one molecule, at least two functional groups having reactivity with expoxy group, carboxyl group or hydroxyl group.

U.S. Patent 5,206,291 describes compositions comprising a polyester containing 1,4-cyclohexanedimethanol residues and an ethylene/GMA copolymer. Stewart et al., *Polymer Engineering and Science,* 33 (11), 675 (1993), discloses that PET containing antimony catalyst residues reacts faster with an ethylene/GMA copolymer than does PET catalyzed by other metals. U.S. Patent 5,436,296 discloses that an ethylene/GMA copolymer may be used to compatibilize blends of polyethylene and polyester. U.S. Patents 5,483,001, 5,407,999, and 5,208,292 and *Die Angewandte Makromolekulare Chemie*, p. 89, disclose polyester compositions having improved toughness which contain an ethylene/alkyl acrylate/GMA terpolymer, an ethylene/alkyl acrylate/maleic anhydride terpolymer. and a catalyst such as dimethylstearylamine which

accelerates the reaction between the functional groups of the two terpolymers.

The following patents describe the use of phosphorus-containing compounds to improve the reaction of epoxy-containing polymers with polyesters. U.S. Patent 4,845,169 and the *Journal of Applied Polymer Science*, 1996, 1957, describe a thermoplastic blend of PET, a polyester elastomer, and 2 to 6 weight percent of an alkyl-aryl phosphite to allow grafting between the two polyesters. U.S. Patent 5,194,468 discloses the use of a mixture of two aromatic phosphites to transesterify a polyester elastomer to a polyester and improve compatibility to a high density polyethylene. U.S. Patent 5,411,999 discloses compositions comprising a polycarbonate, an epoxy-functionalized polyester, a rubbery impact modifier and a catalyst quencher such as sodium dihydrogen phosphate to inhibit transesterification between the polycarbonate and the polyester. Sodium acid pyrophosphate gave the best hydrolytic stability. An alkyl phosphite was found to give very poor hydrolytic stability. U.S. Patent 5,541,244 teaches that phosphates, in particular zinc dihydrogen phosphate, are good transesterification inhibitors that do not negatively influence the impact strength of a mixture of two polyesters. No impact modifiers containing the epoxide functionality are discussed.

Summary of the Invention

Ovenable food trays of the present invention exhibit greatly improved low temperature toughness, i.e., resistance to breaking or fracturing. The food trays are made from certain polyester compositions containing an epoxy-containing impact modifying polymer and are fabricated by conventional thermoforming techniques from extruded sheet material of the polyester compositions. The food trays are characterized by a high degree of crystallinity, e.g., between about 22 and 35% as measured by differential scanning calorimetry (DSC) and an impact strength of at least 3 Joules

when measured by instrumented falling dart at a temperature of -34°C on a 500 micron-thick sample (ASTM D3763). An impact strength of greater than 6 joules when measured by instrumented falling dart at a temperature of -34°C on a 500 micron-thick sample (ASTM D3763) is preferred.

The present invention therefore provides novel articles such as food trays shaped from sheet material, e.g., sheet having a thickness of about 300 to 1000 microns, extruded from a crystallizable polyester composition comprising:

I. about 75 to 98 weight percent of a thermoplastic polyester comprised of:
   (A) diacid residues comprising at least 90 mole percent terephthalic acid residues, 2,6-napthalenedicarboxylic acid residues or a mixture of terephthalic acid and 2,6-naphthalenedicarboxylic acid residues; and
   (B) diol residues comprising at least 90 mole percent diol residues derived from an alkylene glycol containing 2 to 6 carbon atoms or 1,4-cyclohexanedimethanol; and

II. about 25 to 2 weight percent of an impact modifying polymer comprised of about 0.5 to 15 weight percent of epoxy-containing residues derived from monomers selected from glycidyl methacrylate, glycidyl acrylate, allyl glycidyl ether, 3,4-epoxy-1-butene, or a mixture of any two or more of such monomers;

wherein polyester component I is based on 100 mole percent diacid residues and 100 mole percent diol residues and the weight percentages are based on the total weight of components I and II. We also have found that the addition of the epoxy component II improves the crystallization rate of sheet extrude from the polyester composition. While the primary focus of the present invention is directed to food trays, the advantages and principles inherent in the present invention may be utilized for other shaped articles for which an increase in toughness (impact strength) is desired or required.

Detailed Description of the Invention

The polyester material which may be used in the present invention may be any polyester that will crystallize during thermoforming of the food tray although unmodified poly(ethylene terephthalate) is particularly preferred. For example, the crystallizable polyesters also may be selected from poly(propylene terephthalate), poly(tetramethylene terephthalate), poly(methylpentamethylene terephthalate), poly(1,4-cyclohexylenedimethylene terephthalate), poly(ethylene 2,6-naphthalenedicarboxylate), poly(propylene 2,6-naphthalenedicarboxylate), and poly(tetramethylene 2,6-naphthalenedicarboxylate).

The polyester component of our novel compositions are commercially available and/or may be prepared by batch or continuous processes using conventional melt phase or solid state condensation procedures well known in the art. Also, the polyester component may be obtained from post consumer waste, e.g., recycled polyester. Polyesters useful in the present invention are comprised of diacid residues comprising at least 90 mole percent terephthalic acid residues or 2.6-napthalenedicarboxylic acid residues; (B) diol residues comprising at least 90 mole percent residues derived from an alkylene glycol containing 2 to 6 carbon atoms or 1,4-cyclohexanedimethanol; wherein the polyester is made up of 100 mole percent diacid residues and 100 mole percent diol residues. Up to 10 mole percent of the diacid component of the polyesters may be derived from diacids other than terephthalic and 2,6-napthalenedicarboxylic acid residues. For example, up to 10 mole percent of the diacid residues may be residues derived from dicarboxylic acids containing about 4 to about 40 carbon atoms such as succinic, glutaric, adipic, pimelic, suberic, azelic, sebacic, terephthalic, isophthalic, sulfodibenzoic, sulphoisophthalic, maleic, fumaric, 1,4-cyclohexanedicarboxylic (cis-, trans-, or cis/trans mixtures), and the like. The diacid residues may be derived from the

dicarboxylic acids, esters and acid chlorides thereof, and, in some cases, anhydrides thereof.

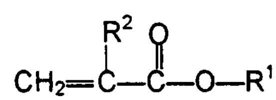
Similarly, up to 10 mole percent of the diol residues may be derived from diols other than residues derived from an alkylene glycol containing 2 to 6 carbon atoms or 1,4-cyclohexanedimethanol. Examples of other diols which may be used in the preparation of the polyester component include 1,8-octanediol, 2,2,4,4-tetramethyl-1,3-cyclobutanediol, diethylene glycol and the like. Small amounts, e.g., up to 2 mole percent, of a branching agent such as trimellitic anhydride, pyromellitic dianhydride, glycerol, pentaerythritol, polyvinyl alcohol, styrene-maleic anhydride (SMA) and the like may be may be included in the polyester if desired. Normally, the permissible amount of diacid residues other than terephthalic acid residues or 2,6-napthalenedicarboxylic acid residues plus diol residues other than residues derived from an alkylene glycol containing 2 to 6 carbon atoms or 1,4-cyclohexanedimethanol will not exceed 10 mole percent of the total of 100 mole percent diacid residues and 100 mole percent diol residues. It is essential that the polyester component crystallize upon being extruded into sheet and thermoformed. The polyester component should have an inherent viscosity (IV) in the range of about 0.4 to about 1.2 dL/g, preferably about 0.55 to 0.95 dL/g, measured at 23°C by dissolving 0.50 g of polyester into 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetrachloroethane. The polyester component of our novel compositions preferably consists essentially of terephthalic acid residues and ethylene glycol residues and has an IV of about 0.55 to 0.95 dL/g.

The second component of the compositions of the present invention is an impact modifying polymer comprised of about 0.5 to 20 weight percent of epoxy-containing residues derived from monomers selected from glycidyl methacrylate, glycidyl acrylate, allyl glycidyl ether, 3,4-epoxy-1-butene, or a mixture of any two or more of such monomers. These epoxy containing monomers may be introduced into the impact modifier during

polymerization, or they may be subsequently grafted onto the impact modifier. Such epoxy-containing impact modifiers are well known in the art and are available from a plurality of manufacturers. Impact modifiers that may be modified with a functional epoxy group include, but are not restricted to, polyethylene; polypropylene; polybutene; ethylene based copolymers and terpolymers containing vinyl acetate, alkyl acrylate, alkyl methacrylate where the alkyl group could be methyl, ethyl, butyl or ethylhexyl; ethylene-propylene copolymers (EPR); ethylene-propylene-diene (EPDM); natural rubber; polybutadiene; polyisoprene; acrylonitrile-butadiene (nitrile rubber); styrene-butadiene (SBR); styrene-butadiene-styrene (SBS); styrene-ethylene-butene-styrene (SEBS); acrylonitrile-butadiene-styrene (ABS); methyl methacrylate-butyl acrylate (acrylic core-shell); methyl methacrylate-butadiene-styrene (MBS core-shell); organic silicone rubbers; elastomeric fluorohydrocarbons; elastomeric polyesters; polyurethanes; or combinations thereof. Of these materials, those based on polyethylene are preferred.

Preferred epoxy-containing impact modifiers comprise copolymers and terpolymers having the respective general formulas E/Y and E/X/Y wherein:

X represents residues derived from



wherein R^1 is alkyl of up to about 8 carbon atoms, preferably alkyl of 1 to 4 carbon atoms, and R^2 is hydrogen, methyl or ethyl, preferably hydrogen or methyl, and X constitutes about 10 to 40 weight percent, preferably 15 to 35 weight percent, and most preferably 20 to 35 weight percent, of terpolymer E/X/Y;

Y represents residues derived from glycidyl methacrylate, glycidyl acrylate, allyl glycidyl ether, or 3,4-epoxy-1-butene which constitute about

0.5 to 20 weight percent, preferably about 2 to 10 weight percent, of copolymer E/Y or terpolymer E/X/Y; and

E represents ethylene residues which constitute the remainder of copolymer E/Y and terpolymer E/X/Y. Of these, copolymers based on ethylene-GMA (E/GMA) containing about 2 to 10 weight percent GMA residues, and terpolymers based on ethylene-methyl acrylate-GMA, ethylene-ethyl acrylate-GMA and ethylene-butyl acrylate-GMA containing about 20 to 35 weight percent alkyl acrylate residues and about 2 to 10 weight percent GMA residues are particularly preferred. Of these, copolymers and terpolymers with melt flow index values between 0.2 and 50 g/10 minutes are preferred. The concentration of the epoxy-containing impact modifiers in the compositions from which the food trays of the present invention are fabricated preferably is about 2 to 15 weight percent, based on the total weight of components I and II.

A second embodiment of the present invention is based on the discovery that the catalyst used in the synthesis of the polyester may affect the toughness of blends of the catalyst residue-containing polyester and an epoxy-containing impact modifier. Polyesters typically are prepared using metal catalysts that remain in the polyester product. Examples of these catalysts include organic and inorganic compounds of arsenic, cobalt, tin, antimony, zinc, titanium, magnesium, gallium, germanium, sodium, lithium and the like. Antimony compounds frequently are used in the preparation of PET. U.S. Patent 4,284,540 notes that antimony catalyst residues are preferred for promoting the reaction between polyester end groups and an epoxy group. Stewart et al., *Polymer Engineering and Science*, 33, (11), 675 (1993) came to the same conclusion after quantifying the rate of reaction between PET and an ethylene/GMA copolymer as a function of PET catalyst.

It is often implied by those knowledgeable in the art that a rapid reaction between the E/GMA and the PET containing residual antimony

catalyst should lead to better dispersion of the E/GMA (i.e., a smaller particle size) and better bond to the PET. This superior dispersion should, in turn, lead to improved toughness in the resultant blend. Furthermore, since the PET containing residual antimony catalyst reacts faster than the PET containing other catalysts, it is implied that the use of PET containing antimony catalyst residues should lead to tougher blends with epoxy containing ethylene copolymers.

In apparent contradiction to the prior art cited above, we have found that when epoxide-containing ethylene polymers are used in antimony-catalyzed PET, they produce lower toughness values than if they are used in titanium catalyzed PET. Apparently, the antimony catalyst residues present in the PET accelerate an epoxy – epoxy reaction of the epoxide-containing polyethylene polymer which crosslinks the polymer into large particle greater than 1 micron in size. These particles are too large to produce maximum toughness in the PET sheet.

In contrast, we have found that good toughness is observed in compositions comprising epoxy-containing impact modifiers and certain polyesters that contain (i) titanium and/or germanium or (ii) antimony and at least one phosphorus compound. Thus, a second embodiment of the present invention pertains to novel shaped articles such as food trays fabricated from sheet material extruded from a crystallizable polyester composition comprising:

I. about 75 to 98 weight percent of a thermoplastic polyester comprised of:
   (A) diacid residues comprising at least 90 mole percent terephthalic acid residues, 2,6-napthalenedicarboxylic acid residues or a mixture of terephthalic acid and 2,6-naphthalenedicarboxylic acid residues;
   (B) diol residues comprising at least 90 mole percent diol residues derived from an alkylene glycol containing 2 to 6 carbon atoms or 1,4-cyclohexanedimethanol; and

(C) at least 25 parts per million by weight (ppmw) of a metal selected from titanium, germanium, or a mixture thereof; and

II. about 25 to 2 weight percent of an impact modifying polymer comprised of about 0.5 to 15 weight percent of epoxy-containing residues derived from monomers selected from glycidyl methacrylate, glycidyl acrylate, allyl glycidyl ether, 3,4-epoxy-1-butene, or a mixture of any two or more of such monomers

wherein polyester component I is based on 100 mole percent diacid residues and 100 mole percent diol residues, the weight percentages are based on the total weight of components I and II.

The polyester component of this novel composition contains at least 25 ppmw of a metal selected from Ti, Ge or a mixture thereof, typically about 25 to 200 ppmw and preferably about 50 to 100 ppmw Ti, Ge or a mixture thereof. The metal preferably is titanium. The titanium and germanium may be introduced to the polyester by using a titanium and/or germanium compound as a catalyst in the preparation of the polyester. It is also possible to introduce the titanium and/or germanium into the polyester subsequent to the preparation of the polyester. The polyester compositions of this embodiment of the present invention are substantially and essentially free of antimony, e.g., the polyester compositions contain less than 20 ppmw antimony, preferably no detectable antimony.

A third embodiment of the present invention pertains to novel shaped articles, especially food trays, fabricated from sheet material extruded from a crystallizable polyester composition comprising:

I. about 75 to 98 weight percent of a thermoplastic polyester comprised of:

(A) diacid residues comprising at least 90 mole percent terephthalic acid residues, 2,6-napthalenedicarboxylic acid residues or a mixture of terephthalic acid and 2,6-naphthalenedicarboxylic acid residues;

(B) diol residues comprising at least 90 mole percent diol residues derived from an alkylene glycol containing 2 to 6 carbon atoms or 1,4-cyclohexanedimethanol; and

(C) at least 50 parts per million by weight (ppmw) antimony metal;

II. about 25 to 2 weight percent of an impact modifying polymer comprised of about 0.5 to 15 weight percent of epoxy-containing residues derived from monomers selected from glycidyl methacrylate, glycidyl acrylate, allyl glycidyl ether, 3,4-epoxy-1-butene, or a mixture of any two or more of such monomers; and

III. a phosphorus compound;

wherein polyester component I is based on 100 mole percent diacid residues and 100 mole percent diol residues, the weight percentages are based on the total weight of components I and II, and the amount of phosphorus compound present gives a P:Sb atomic ratio of 1:1 or greater.

The thermoplastic polyester and impact modifying polymer components of the third embodiment of the present invention are the same as those described above except that the polyester contains at least 50 ppmw antimony. The polyester component typically contains about 50 to 400 ppmw Sb and preferably about 100 to 300 ppmw Sb. The antimony metal may be introduced to the polyester by using an antimony compound, e.g., antimony trioxide or an antimony carboxylate salt such as antimony acetate, as a catalyst in the preparation of the polyester. It is also possible to introduce the antimony into the polyester subsequent to the preparation of the polyester.

The third component of third embodiment compositions comprises at least one phosphorus compound which is present in an amount which gives a P:Sb atomic ratio of at least 1:1. The particular phosphorus compound is not critical and may be selected from a wide variety of phosphorus-containing compounds such as organo-phosphorus compounds, e.g., phosphite esters such as trihydrocarbyl phosphites, phosphonate

esters such as dihydrocarbyl phosphonates, phosphate esters such as trihydrocarbyl phosphates, phosphines such as trihydrocarbyl phosphines, phosphine oxides such as trihydrocarbylphosphine oxides and the like, wherein the hydrocarbyl groups may be selected from alkyl, cycloalkyl and aryl groups containing up to about 20 carbon atoms. A preferred phosphorus compound is bis(2,4-tertiary-butylphenyl)pentaerythritol diphosphite available under the tradenames Ultranox 626 and Alkanox P-24. Additional examples of specific organo-phosphorus compounds include distearylpentaerythritol diphosphite available under the tradenames Weston 618 and Mark 5060, tetrakis(2,4-di-t-butylphenyl)4,4'-biphenylene-diphosphonite available under the tradenames Sandostab P-EPQ and Alkanox 24-44, triphenyl phosphate, triphenyl phosphite, and dimethyl-phosphonate available under the tradenames Antiblaze 1045 and Amgard P-45. Phosphorus acids such as phosphorous acid, phosphoric acid, pyrophosphoric acid, polyphosphoric acid and their respective salts also may be sued. All of these phosphorus compounds are believed to be effective in slowing the epoxy – epoxy reaction due to a phosphorus-induced inactivation of the residual antimony catalyst. Inactivation of the antimony permits a selective reaction between the epoxy portion of the impact modifying polymer and the polyester which results in a better dispersion and thus, better impact modification.

The amount of phosphorus compound present in the polyester compositions of the third embodiment of our invention normally should be an amount which gives a P:Sb atomic ratio of 1:1 or greater, e.g., a P:Sb atomic ratio in the range of about 1:1 to 5:1, preferably in the range of 2:1 to 3:1. The inclusion of excessive amounts of phosphorus compounds in the polyester compositions can result in compositions having poor impact properties even though the impact modifier is present as small dispersions. Excessive phosphorus compounds (of various oxidation states) can form strong acids by combination with trace amounts of water present in even

the most thoroughly dried polyester. Such strong acids are detrimental to polyester molecular weight (M_W) upon which toughness depends directly. Strong acids also can catalyze epoxy-epoxy reactions that may lessen adhesion to the matrix.

The phosphorus compound normally is added to the molten polyester simultaneously with or prior to the addition of the epoxy-containing impact modifier. The phosphorous compound also may be added to the polyester during its manufacture although adding the phosphorus compound during polyester preparation may have a negative effect on the rates of polymerization and/or solid stating. Thus, addition of a phosphorus compound during polymerization is a not a preferred method of addition.

Once the impact modifier has been blended into and reacted with the polyester, extruded pellets of the resultant blend may be further combined with additional polyester in a subsequent sheet extrusion or compounding step. If this is done, there is no restriction on catalyst residues present in the polyester that is added in this subsequent step. The catalyst residues only affect the initial reaction between the impact modifier and the polyester.

The impact modifier and polyester may be pellet blended before extrusion or they may be fed from separate streams. These reactive impact modifiers also may be combined with non-reactive impact modifiers of similar composition. The polyester compositions of this invention can be readily prepared by conventional compounding technology, such as the use of single or twin screw extruders. The resultant blends are readily extruded into film or sheeting and injection molded, compression molded or thermoformed into desired shapes or objects.

Other additives normally used in polyesters such as stabilizers, antioxidants, pigments, colorants, plasticizers, flame retardants, mold release agents, slip agents and the like may be used as desired. Glass

fibers or other inorganic fillers can also be included. Although not required, small amounts of nucleating agents such as polyethylene, polypropylene, talc and the like may be used.

A particularly preferred embodiment of the invention consists of food trays fabricated from sheet material having a thickness of about 300 to 1000 microns extruded from a crystallizable polyester composition comprising:

I. about 85 to 98 weight percent of a thermoplastic polyester comprising poly(ethylene terephthalate) having an inherent viscosity of about 0.55 to 0.95 dL/g, measured at 25°C using 0.50 g of polyester per 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetrachloroethane; and

II. about 15 to 2 weight percent of an impact modifying polymer selected from ethylene/methyl acrylate/glycidyl methacrylate terpolymers containing about 20 to 35 weight percent methyl acrylate residues and about 2 to 10 weight percent glycidyl methacrylate residues;

wherein the weight percentages are based on the total weight of components I and II.

Another particularly preferred embodiment consists of food trays fabricated from sheet material having a thickness of about 300 to 1000 microns extruded from a crystallizable polyester composition comprising:

I. about 85 to 98 weight percent of a thermoplastic polyester comprising poly(ethylene terephthalate) having an inherent viscosity of about 0.55 to 0.95 dL/g, measured at 25°C using 0.50 g of polyester per 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetrachloroethane, containing about 50 to 100 ppmw Ti; and

II. about 15 to 2 weight percent of an impact modifying terpolymer selected from ethylene/methyl acrylate/glycidyl methacrylate terpolymers containing about 20 to 35 weight percent methyl acrylate residues and about 2 to 10 weight percent glycidyl methacrylate residues;

wherein the weight percentages are based on the total weight of components I and II.

Yet another particularly preferred embodiment consists of food trays fabricated from sheet material having a thickness of about 300 to 1000 microns extruded from a crystallizable polyester composition comprising:

I. about 85 to 98 weight percent of a thermoplastic polyester comprising poly(ethylene terephthalate) having an inherent viscosity of about 0.55 to 0.95 dL/g, measured at 25°C using 0.50 g of polyester per 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetrachloroethane, containing about 100 to 300ppmw Sb;

II. about 15 to 2 weight percent of an impact modifying terpolymer selected from ethylene/methyl acrylate/glycidyl methacrylate terpolymers containing about 20 to 35 weight percent methyl acrylate residues and about 2 to 10 weight percent glycidyl methacrylate residues; and

III. a phosphorus compound;

wherein the weight percentages are based on the total weight of components I and II and the amount of phosphorus compound present gives a P:Sb atomic ratio of about 2:1 to 3:1.

The shaped articles of the present invention are fabricated from sheet material having a thickness of about 300 to 2000 microns, preferably about 400 to 750 microns, which has been extruded according to known procedures and using conventional extrusion equipment. The food trays are fabricated using conventional thermoforming techniques and have a thickness of about 300 to 2000 microns, preferably about 400 to 750 microns. The food trays typically consist of a bottom or floor with upwardly extending sidewalls having a height of about 1 to 10 cm and a formed upper lip designed to receive a lid or other closure to provide an hermetically sealed container.

Typically, in the glass-to-mold process, the sheet is prepared by extruding at a melt temperature above 260°C and then immediately

quenching the sheet to a temperature below about 75°C to fix the sheet in an amorphous state. A tray blank is then cut from this amorphous sheet and reheated, typically to about 140°C to 170°C and formed into the tray shape in a thermoforming mold. The sheet may conform to the mold either through the application of a vacuum, pressure, or through matched molds. The formed sheet is allowed to remain in the mold from between 4 to 10 seconds to allow the amorphous sheet to crystallize, and is then removed from the mold. The melt-to-mold process is similar, except that the extruded polymer is never quenched to below 75°C, but rather the molten sheet is extruded directly onto the molds. The entire melt-to-mold process is, therefore, continuous.

In general, food trays must possess good low temperature toughness to resist breakage from accidental falls during storage or transportation. They must also retain reasonable strength and dimensional stability over a range of temperatures from –34°C to about 230°C. They must also resist distortion and yellowing at these elevated temperatures and should resist torsion or flexion sufficiently to allow removal or a hot tray and contents from an oven without sagging and spilling the contents.

Examples

The food trays provided by the present invention and their preparation are further illustrated by the following examples wherein all percentages given are by weight unless otherwise specified. The crystallizable polyester component of the polyester compositions prepared was a poly(ethylene terephthalate) having an IV of 0.95 dL/g prepared from ethylene glycol and terephthalic acid using 200 ppmw antimony catalyst provided as antimony triacetate, except as noted in Example 2. The impact modifiers used were:

Impact Modifier A: a butyl acrylate core/methyl methacrylate shell core/shell impact modifier (PARALOID EXL 5475 from Rohm and Haas).

Impact Modifier B: a random copolymer of ethylene and 24% methyl acrylate having a melt index of 7 g/10 minutes (LOTRYL 24MA07 from Elf Atochem).

Impact Modifier C: a butadiene core/styrene-acrylonitrile shell core/shell impact modifier (BLENDEX 338 from GE Specialty Chemicals Division).

Impact Modifier D: a random terpolymer of ethylene, 23.5% methyl acrylate and 7.25% glycidyl methacrylate having a melt index of 6.5 g/10 minutes (LOTADER AX8900 from Elf Atochem).

Impact Modifier E: a random copolymer of ethylene and 8% glycidyl methacrylate having a melt index of 6.5 g/l0 minutes (LOTADER AX8840 from Elf Atochem).

Impact Modifier F: a butadiene-styrene core/methyl methacrylate shell (MBS) core/shell impact modifier (PARALOID 3647 from Rohm and Haas).

The crystallizable polyester compositions used in the examples were prepared by a two-step process. First, a concentrate containing 20% of an impact modifier, optionally with the phosphorus compound bis(2,4-tertiary-butylphenyl)pentaerythritol diphosphite (Ultranox 626), was prepared using a Sterling 1.25 inch (32 mm) single screw extruder operated at 80 revolutions per minute (RPM) and a 280°C (536°F) melt temperature. The

PET, impact modifier, and phosphorus compound were all added simultaneously into the main hopper of the extruder. Both the PET and impact modifiers were dried in dessicant bed driers prior to compounding.

The pellets produced by the extruder were then bag blended together with an additional 1.425 parts virgin PET and 0.075 parts of a linear low density polyethylene nucleating agent (LLDPE; TENITE E3031-81aa from Eastman Chemical Company). These pellet blends were dried for 16 hours at 100°C (212°F) and subsequently extruded into 0.025 inch (635 microns) thick film on a Killion 1.5 inch (38 mm) single screw extruder operated at 75 RPM and a 280°C (536°F) melt temperature. The casting roll was maintained at a constant temperature of 65°C (150°F) to effectively quench the film. By using this two step process for preparing sheet, the concentrate pellets experienced a second heat history, similar to the common practice of using 30% to 60% regrind when extruding crystalline PET film.

The extruded sheet material subsequently was thermoformed into food trays using a 160°C (320°F) mold temperature and a 10 second in-mold cycle. Differential scanning calorimetry (DSC) was used to confirm that the polyester compositions in the trays had attained the desirable crystallinity level of 22-35% during thermoforming. The thermoformed food trays consisted of a bottom having the dimensions 10 by 15 cm and sidewalls approximately 3 cm in height. The bottom and sidewalls were approximately 600 micron thick.

The low temperature toughness of the thermoformed food trays was determined using 10 by 10 cm (4 by 4 inch) samples having a thickness of 600 microns cut from the bottom of thermoformed crystalline trays and cooled in a freezer at -34°C (–29°F). After at least 4 hours in the freezer. the samples were transferred to a Ceast falling dart impact tester whose chamber had also been cooled to –34°C (–29°F). The specimens were individually struck with a 22.5 kg tup travelling at 3.3 meters per second

according to the procedure of ASTM D3763. The impact energy values listed in the examples represent the total energy absorbed by the sample up to the point of either fracture of the sample or puncture by the tup.

The crystallization rate halftimes of the amorphous sheet material having a thickness of 600 microns were measured by differential scanning calorimetry (DSC) at 120°C (248°F). The measured halftime is the time required to obtain 50% of the total crystallinity found in the sheet. Shorter halftimes indicate faster rates.

COMPARATIVE EXAMPLE 1

A food tray was thermoformed from a sheet extruded from a composition consisting of PET and only 3% LLDPE crystallization aid. The bottom of the tray had a failure impact energy of 1.02 joules (1.38 foot-pounds). The composition had a DSC halftime at 120°C (248°F) of 1.33 minutes.

COMPARATIVE EXAMPLE 2

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 8% Impact Modifier A and 3% LLDPE crystallization aid. The bottom of the tray had a failure impact energy of 3.05 joules (4.14 foot-pounds). The composition had a DSC halftime at 120°C (248°F) of 1.33 minutes.

COMPARATIVE EXAMPLE 3

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 15% Impact Modifier B and 3% LLDPE crystallization aid. The bottom of the tray had a failure impact energy of 0.75 joules (1.02 foot-pounds). The composition had a DSC halftime at 120°C (248°F) of 1.27 minutes.

COMPARATIVE EXAMPLE 4

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 8% Impact Modifier C and 3% LLDPE crystallization aid. The bottom of the tray had a failure impact energy of 2.96 joules (4.02 foot-pounds).

EXAMPLE 1

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 8% Impact Modifier D and 3% LLDPE crystallization aid. The bottom of the tray had a failure impact energy of 5.06 joules (6.87 foot-pounds). The composition had a DSC halftime at 120°C (248°F) of 1.07 minutes. This crystallization rate is significantly faster than those shown in the comparative examples.

EXAMPLE 2

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 8% Impact Modifier D and 3% LLDPE crystallization aid. The PET used to make this concentrate with the impact modifier in this example was a poly(ethylene terephthalate) having an IV of 0.72 which was prepared from ethylene glycol and terephthalic acid using 100 ppmw titanium catalyst provided as titanium tetraisoprooxide. This PET was subsequently blended with additional PET having an IV of 0.95 prepared from ethylene glycol and terephthalic acid using 200 ppmw antimony catalyst provided as antimony triacetate. The bottom of the tray had a failure impact energy of 6.63 joules (8.95 foot-pounds).

EXAMPLE 3

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 8% Impact Modifier D, 3% LLDPE crystallization aid and 0.05% bis(2,4-tertiary-butylphenyl)pentaerythritol

diphosphite. The bottom of the tray had a failure impact energy of 9.06 joules (12.30 foot-pounds).

EXAMPLE 4

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 8% Impact Modifier E, 3% LLDPE crystallization aid and 0.05% bis(2,4-tertiary-butylphenyl)pentaerythritol diphosphite. The bottom of the tray had a failure impact energy of 8.91 joules (12.00 foot-pounds).

EXAMPLE 5

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 4% Impact Modifier D, 4% Impact Modifier B and 3% LLDPE crystallization aid. The bottom of the tray had a failure impact energy of 3.42 joules (4.64 foot-pounds).

EXAMPLE 6

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 4% Impact Modifier D, 4% Impact Modifier B, 3% LLDPE crystallization aid and 0.05% bis(2,4-tertiary-butylphenyl)pentaerythritol diphosphite. The bottom of the tray had a failure impact energy of 8.73 joules (11.86 foot-pounds).

COMPARATIVE EXAMPLE 5

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 15% Impact Modifier B, 3% LLDPE crystallization aid and 0.05% bis(2,4-tertiary-butylphenyl)pentaerythritol diphosphite. The bottom of the tray had a failure impact energy of 0.42 joules (0.57 foot-pounds).

EXAMPLE 7

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 2% Impact Modifier D, 6% Impact Modifier A and 3% LLDPE crystallization aid. The bottom of the tray had a failure impact energy of 8.52 joules (11.57 foot-pounds).

EXAMPLE 8

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 2% Impact Modifier E, 6% Impact Modifier A and 3% LLDPE crystallization aid. The bottom of the tray had a failure impact energy of 5.66 joules (7.68 foot-pounds).

EXAMPLE 9

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 2% Impact Modifier D, 6% Impact Modifier F and 3% LLDPE crystallization aid. The bottom of the tray had a failure impact energy of 8.17 joules (11.10 foot-pounds).

EXAMPLE 10

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 2% Impact Modifier E, 6% Impact Modifier F and 3% LLDPE crystallization aid. The bottom of the tray had a failure impact energy of 7.93 joules (10.77 foot-pounds).

EXAMPLE 11

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 2% Impact Modifier D, 6% Impact Modifier C and 3% LLDPE crystallization aid. The bottom of the tray had a failure impact energy of 4.53 joules (6.15 foot-pounds).

EXAMPLE 12

A food tray was thermoformed from a sheet extruded from a composition consisting of PET, 2% Impact Modifier D, 6% Impact Modifier C, 3% LLDPE crystallization aid and 0.05% bis(2,4-tertiary-butylphenyl)-pentaerythritol diphosphite. The bottom of the tray had a failure impact energy of 6.51 joules (8.84 foot-pounds).

EXAMPLE 13

A sheet was extruded from a composition consisting of PET and 8% Impact Modifier D. The composition had a DSC halftime at 120°C (248°F) of 1.20 minutes. This halftime is faster than that for PET containing only 3% LLDPE crystallization aid (Comparative Example 1) indicating that the LLDPE crystallization aid is not required at this level of impact modifier to obtain sufficient crystallization rate.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.

Claims

We claim:

1. An article shaped from sheet material extruded from a crystallizable polyester composition comprising:

I. about 75 to 98 weight percent of a thermoplastic polyester comprised of:

(A) diacid residues comprising at least 90 mole percent terephthalic acid residues, 2,6-napthalenedicarboxylic acid residues or a mixture of terephthalic acid and 2,6-naphthalenedicarboxylic acid residues; and

(B) diol residues comprising at least 90 mole percent diol residues derived from an alkylene glycol containing 2 to 6 carbon atoms or 1,4-cyclohexanedimethanol; and

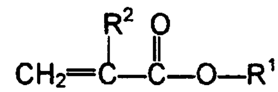
II. about 25 to 2 weight percent of an impact modifying polymer comprised of about 0.5 to 20 weight percent of epoxy-containing residues derived from monomers selected from glycidyl methacrylate, glycidyl acrylate, allyl glycidyl ether, 3,4-epoxy-1-butene, or a mixture of any two or more of such monomers;

wherein component I is based on 100 mole percent diacid residues and 100 mole percent diol residues and the weight percentages are based on the total weight of components I and II.

2. An article according to Claim 1 which has been thermoformed from sheet material having a thickness of about 300 to 1000 microns wherein the polyester has an inherent viscosity (IV) in the range of about 0.4 to about 1.2 dL/g measured at 23°C by dissolving 0.50 g of polyester into 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetrachloroethane.

3. An article according to Claim 2 wherein the article is a food tray, the polyester has an inherent viscosity (IV) in the range of about 0.55 to 0.95 dL/g and the impact modifying polymer is selected from copolymers and terpolymers having the respective general formulas E/Y and E/X/Y wherein:

X represents residues derived from



wherein R^1 is alkyl of up to about 8 carbon atoms, and R^2 is hydrogen, methyl or ethyl, and X constitutes about 10 to 40 weight percent of terpolymer E/X/Y;

Y represents residues derived from glycidyl methacrylate, glycidyl acrylate, allyl glycidyl ether, or 3,4-epoxy-1-butene which constitute about 0.5 to 20 weight percent of copolymer E/Y or terpolymer E/X/Y; and

E represents ethylene residues which constitute the remainder of copolymer E/Y and terpolymer E/X/Y.

4. An article shaped from sheet material extruded from a crystallizable polyester composition comprising:

I. about 75 to 98 weight percent of a thermoplastic polyester comprised of:
   (A) diacid residues comprising at least 90 mole percent terephthalic acid residues, 2,6-napthalenedicarboxylic acid residues or a mixture of terephthalic acid and 2,6-naphthalenedicarboxylic acid residues;
   (B) diol residues comprising at least 90 mole percent diol residues derived from an alkylene glycol containing 2 to 6 carbon atoms or 1,4-cyclohexanedimethanol; and
   (C) at least 25 parts per million by weight (ppmw) of a metal selected from titanium, germanium, or a mixture thereof; and

II. about 25 to 2 weight percent of an impact modifying polymer comprised of about 0.5 to 20 weight percent of epoxy-containing residues derived

from monomers selected from glycidyl methacrylate, glycidyl acrylate, allyl gycidyl ether, 3,4-epoxy-1-butene, or a mixture of any two or more of such monomers;

wherein component I is based on 100 mole percent diacid residues and 100 mole percent diol residues and the weight percentages are based on the total weight of components I and II.

5. An article according to Claim 4 which has been thermoformed from sheet material having a thickness of about 300 to 1000 microns wherein the polyester contains about 25 to 200 ppmw of a metal selected from titanium, germanium or a mixture thereof and the polyester has an inherent viscosity (IV) in the range of about 0.4 to about 1.2 dL/g measured at 23°C by dissolving 0.50 g of polyester into 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetrachloroethane.

6. An article according to Claim 5 wherein the article is a food tray, the polyester contains about 50 to 100 ppmw of a metal selected from titanium, germanium or a mixture thereof, the polyester has an inherent viscosity (IV) in the range of about 0.55 to 0.95 dL/g and the impact modifying polymer is selected from from copolymers and terpolymers having the respective general formulas E/Y and E/X/Y wherein:

X represents residues derived from

$$CH_2{=}\overset{\overset{\displaystyle R^2}{|}}{C}-\overset{\overset{\displaystyle O}{\|}}{C}-O-R^1$$

wherein R^1 is alkyl of up to about 8 carbon atoms, and R^2 is hydrogen, methyl or ethyl, and X constitutes about 10 to 40 weight percent of terpolymer E/X/Y;

Y represents residues derived from glycidyl methacrylate, glycidyl acrylate, allyl glycidyl ether, or 3,4-epoxy-1-butene which constitute about 0.5 to 20 weight percent of copolymer E/Y or terpolymer E/X/Y; and

E represents ethylene residues which constitute the remainder of copolymer E/Y and terpolymer E/X/Y.

7. An article shaped from sheet material extruded from a crystallizable polyester composition comprising:
   I. about 75 to 98 weight percent of a thermoplastic polyester comprised of:
   (A) diacid residues comprising at least 90 mole percent terephthalic acid residues, 2,6-napthalenedicarboxylic acid residues or a mixture of terephthalic acid and 2,6-naphthalenedicarboxylic acid residues;
   (B) diol residues comprising at least 90 mole percent diol residues derived from an alkylene glycol containing 2 to 6 carbon atoms or 1,4-cyclohexanedimethanol; and
   (C) at least 50 parts per million by weight (ppmw) antimony metal;
   II. about 25 to 2 weight percent of an impact modifying polymer comprised of about 0.5 to 20 weight percent of epoxy-containing residues derived from monomers selected from glycidyl methacrylate, glycidyl acrylate, allyl gycidyl ether, 3,4-epoxy-1-butene, or a mixture of any two or more of such monomers; and
   III. a phosphorus compound;

wherein component I is based on 100 mole percent diacid residues and 100 mole percent diol residues, the weight percentages are based on the total weight of components I and II, and the amount of phosphorus compound present gives a P:Sb atomic ratio of 1:1 or greater.

8. An article according to Claim 7 which has been thermoformed from sheet material having a thickness of about 300 to 1000 microns wherein the polyester contains about 50 to 400 ppmw antimony, the polyester has an inherent viscosity (IV) in the range of about 0.4 to about 1.2 dL/g measured

at 23°C by dissolving 0.50 g of polyester into 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetrachloroethane, and the phosphorus compound is present in an amount which gives a P:Sb atomic ratio in the range of about 1:1 to 5:1.

9. An article according to Claim 8 wherein the article is a food tray, the polyester contains about 100 to 300 ppmw antimony, the polyester has an inherent viscosity (IV) in the range of about 0.55 to 0.95 dL/g and the impact modifying polymer is selected from from copolymers and terpolymers having the respective general formulas E/Y and E/X/Y wherein:

X represents residues derived from

$$CH_2{=}\overset{R^2}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O-R^1$$

wherein R^1 is alkyl of up to about 8 carbon atoms, and R^2 is hydrogen, methyl or ethyl, and X constitutes about 10 to 40 weight percent of terpolymer E/X/Y;

Y represents residues derived from glycidyl methacrylate, glycidyl acrylate, allyl glycidyl ether, or 3,4-epoxy-1-butene which constitute about 0.5 to 20 weight percent of copolymer E/Y or terpolymer E/X/Y; and

E represents ethylene residues which constitute the remainder of copolymer E/Y and terpolymer E/X/Y.

10. A food tray fabricated from sheet material having a thickness of about 400 to 750 microns extruded from a crystallizable polyester composition comprising:

I. about 85 to 98 weight percent of a thermoplastic polyester comprising poly(ethylene terephthalate) having an inherent viscosity of about 0.55 to 0.95 dL/g, measured at 25°C using 0.50 g of polyester per 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetrachloroethane; and

II. about 15 to 2 weight percent of an impact modifying polymer selected from ethylene/glycidyl methacrylate (GMA) copolymers containing about 2 to 10 weight percent GMA residues and ethylene/methyl acrylate/GMA, ethylene/ethyl acrylate/GMA, and ethylene/butyl acrylate/GMA terpolymers containing about 20 to 35 weight percent alkyl acrylate residues and about 2 to 10 weight percent GMA residues;
wherein the weight percentages are based on the total weight of components I and II and the food trays are characterized by a crystallinity between about 22 and 35% as measured by differential scanning calorimetry and an impact strength of greater than 6 Joules when measured by instrumented falling dart at a temperature of -34°C on a 500 micron-thick sample.

11. A food tray fabricated from sheet material having a thickness of about 400 to 750 microns extruded from a crystallizable polyester composition comprising:
I. about 85 to 98 weight percent of a thermoplastic polyester comprising poly(ethylene terephthalate) having an inherent viscosity of about 0.55 to 0.95 dL/g, measured at 25°C using 0.50 g of polyester per 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetrachloroethane, containing about 50 to 100 ppmw Ti; and
II. about 15 to 2 weight percent of an impact modifying polymer selected from ethylene/glycidyl methacrylate (GMA) copolymers containing about 2 to 10 weight percent GMA residues and ethylene/methyl acrylate/GMA, ethylene/ethyl acrylate/GMA, and ethylene/butyl acrylate/GMA terpolymers containing about 20 to 35 weight percent alkyl acrylate residues and about 2 to 10 weight percent GMA residues;
wherein the weight percentages are based on the total weight of components I and II and the food trays are characterized by a crystallinity between about 22 and 35% as measured by differential scanning

calorimetry and an impact strength greater then 6 3 Joules when measured by instrumented falling dart at a temperature of -34°C on a 500 micron-thick sample.

12. A food tray fabricated from sheet material having a thickness of about 400 to 750 microns extruded from a crystallizable polyester composition comprising:

I. about 85 to 98 weight percent of a thermoplastic polyester comprising poly(ethylene terephthalate) having an inherent viscosity of about 0.55 to 0.95 dL/g, measured at 25°C using 0.50 g of polyester per 100 mL of a solvent consisting of 60 weight percent phenol and 40 weight percent tetrachloroethane, containing about 100 to 300 ppmw Sb;

III. about 15 to 2 weight percent of an impact modifying polymer selected from ethylene/glycidyl methacrylate (GMA) copolymers containing about 2 to 10 weight percent GMA residues and ethylene/methyl acrylate/GMA, ethylene/ethyl acrylate/GMA, and ethylene/butyl acrylate/GMA terpolymers containing about 20 to 35 weight percent alkyl acrylate residues and about 2 to 10 weight percent GMA residues; and

III. a phosphorus compound;

wherein the weight percentages are based on the total weight of components I and II, the amount of phosphorus compound present gives a P:Sb atomic ratio of about 2:1 to 3:1 and the food trays are characterized by a crystallinity between about 22 and 35% as measured by differential scanning calorimetry and an impact strength greater than 6 Joules when measured by instrumented falling dart at a temperature of -34°C on a 500 micron-thick sample.

INTERNATIONAL SEARCH REPORT

Inter. ...nal Application No
PCT/US 99/23276

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L67/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 379 (C-463), 10 December 1987 (1987-12-10) & JP 62 146950 A (TORAY IND INC), 30 June 1987 (1987-06-30) abstract	1-3,7-9
Y		5,6, 10-12
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 379 (C-463), 10 December 1987 (1987-12-10) & JP 62 146948 A (TORAY IND INC), 30 June 1987 (1987-06-30)	1-6
Y	abstract	10,11

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 February 2000	07/03/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Dury, O

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Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 11, 30 September 1998 (1998-09-30) & JP 10 158490 A (KANEGAFUCHI CHEM IND CO LTD), 16 June 1998 (1998-06-16)	1-6
Y	abstract	10,11
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 239 (C-367), 19 August 1986 (1986-08-19) & JP 61 072050 A (TORAY IND INC), 14 April 1986 (1986-04-14)	1-6
Y	abstract	10,11
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 379 (C-463), 10 December 1987 (1987-12-10) & JP 62 146949 A (TORAY IND INC), 30 June 1987 (1987-06-30)	1-6
Y	abstract	10,11
X	US 4 284 540 A (IIDA HIROSHI ET AL) 18 August 1981 (1981-08-18)	1-6
Y	column 6, line 45-49; claim 1 column 7, line 10 - line 13; tables 1-3	7-12
X	US 5 208 292 A (HERT MARIUS ET AL) 4 May 1993 (1993-05-04) column 3, line 45; examples 1,5,6	1-12
X	US 5 098 953 A (TOYOSHIMA YOSHIKI ET AL) 24 March 1992 (1992-03-24)	1-3
Y	column 1, line 12 - line 16; claim 1	4-12
Y	STEWART, GEORGE, MILLER, AND PAUL: "Efect of catalyst on the reactive processing of polyesters with epoxy-functional polymers" POLYMER ENGINEERING AND SCIENCE, vol. 33, no. 11, 1993, page 675-685 XP002127429 cited in the application abstract; table 1 page 676	4-12

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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